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Abstract. We measured time-resolved spectra and emission decay times under pulsed X-ray and synchrotron excitation in alkali-earth fluorides doped with Pr^{3+} ions. Two fast decay components were found in the emission spectra of BaF$_2$-Pr^{3+} and SrF$_2$-Pr^{3+} . These were 4 ns and 21 ns in BaF$_2$-Pr^{3+} and 8 and 24 ns in SrF$_2$-Pr^{3+}. The intensity of the faster components 4 ns and 8 ns depended on concentration of Pr^{3+}. Thus, the presence of aggregates might be the cause of such faster components.

1. Introduction

In past two decades materials doped with Ce^{3+} were recognized as good scintillators [1], [2]. Other lanthanide activators have lately gained popularity, one of them being praseodymium Pr. Crystals activated with Pr such as LuAG:Pr^{3+} have demonstrated excellent scintillation properties [3]. Scintillators doped with Pr^{3+}, apart from a high scintillation yield, possess a fast time response (15-30 ns) [4] that makes them promising for application in fast radiation detectors. However, the underlying mechanisms of energy transfer from the primary electron-hole pair (e-h) to the activator ion remain unknown in many wide bandgap materials.

Alkali-earth fluorides activated with lanthanides have been studied for a long time. A nearly absence of slow decay components [5] and an excellent temperature stability of light yield [6] have been proven for BaF$_2$ doped with Pr^{3+} in contrast to the Ce-doped materials. Energy transfer mechanisms in Pr^{3+} and Ce^{3+} doped materials are different [7]. The influence of a charge trapping process on the scintillation mechanism first suggested for YAG:Ce and YAP:Ce [8] has later been considered for cerium doped barium fluoride in [9], [10]. Therefore, alkali-earth fluorides are expected to be good objects for the research of excitation energy transfer processes in scintillators.

In this work we study CaF$_2$, SrF$_2$, and BaF$_2$ crystals doped in a wide range of Pr^{3+} concentrations from 0.015 to 3-5 mol.% using the methods of time-resolved spectroscopy.

2. Experimental methods

The crystals BaF$_2$, SrF$_2$, and CaF$_2$ doped with different concentrations of Pr^{3+} ions were grown in a graphite crucible by the Stockbarger method. Samples of 8x10x2 mm dimensions were used. The excitation was performed with a pulsed X-ray or synchrotron radiation.

The excitation by synchrotron radiation was performed at the SUPERLUMI station of HASYLAB at DESY, Hamburg, Germany (pulse duration below 1 ns). A sample was mounted in a cold-finger helium-flow cryostat. Measurements were performed at 11 K in the two time windows, short 1.5-10.5 ns (STW) and long 114-162 ns (LTW), and in the time-integrated regime. A BM-50 monochromator equipped with a Hamamatsu R2059 photomultiplier was used for luminescence analysis. A more detailed description of the SUPERLUMI station was given by Zimmerer in [11].

The pulsed X-ray excitation was performed with a X-ray tube based on MIRA (pulse duration is about 8 ns). We used a grating monochromator MDR-2, a photomodule Hamamatsu H6780-04 and an oscilloscope Rigol DS1202CA for emission analysis. Experiments were carried out at room temperature (RT) and 78 K. A sample was mounted in a vacuum cryostat. Like in the case of the excitation by synchrotron radiation, the measurements were performed in the two time windows, short 0-12 ns (STW) and long 100-200 ns (LTW), and in the time-integrated regime.

3. Experimental results

3.1. Time-resolved spectra

Time-resolved spectra of Pr doped CaF_2, SrF_2, and BaF_2 crystals under X-ray excitation at 80 K are shown in Figures 1 and 2. The position of the bands in a complicated spectra measured in the STW and time-integrated regime (curves 1 and 3) coincide with those of the *5d-4f* spectral lines observed under synchrotron radiation [12] and optical excitation in Pr^{3+} doped fluorides [13]. This allows us to ascribe also these bands to the *5d-4f* emission.

The wide band at about 3.5 eV in SrF_2-Pr^{3+} detected in the STW and time-integrated regime (Figure 1 (curve 1, panel B)) is related to the singlet exciton emission [14].

In LTW, we found a broad band peaking at about 300 nm in all the investigated crystals.

The intensity of this emission was the highest in pure crystals and decreased with increase of Pr^{3+} concentration in doped crystals, whereas if the Pr^{3+} concentration exceeded 1% the emission at 300 nm was completely absent. The decay time of the 300 nm emission was 600 ns for BaF_2-Pr^{3+} and more than 1 μs for SrF_2-Pr^{3+} and CaF_2-Pr^{3+}. Analogous bands have been assigned to the self-trapped exciton (STE) emission in undoped crystals [15]. In SrF_2-Pr^{3+}, other peaks of low intensity band could be found apart from the STE emission in the energy region of 4-5 eV. In CaF_2-Pr^{3+}, such a structure dominates in the LTW spectrum, being well correspondent to the *5d-4f* emission of Pr^{3+} (compare, e.g., to the STW spectrum of CaF_2-Pr^{3+} in Figure 1 (curve 2, panel A), and Figure 2 (curve 2, panel A)).

The STW emission spectra, measured at room temperature, coincided completely with those measured at 80 K except the quenched singlet exciton band in Pr^{3+} doped strontium fluoride.

In order to clarify the processes of energy transfer to the Pr^{3+} centre in the crystals studied in general and to understand the appearance of the delayed *5d-4f* emission in the LTW in particular, we measured the time-resolved emission spectra of Pr doped crystals under excitation by synchrotron radiation of two energies: in the low-energy bands of Pr^{3+} and in the region of direct excitation of STEs (Figures 3, 4). Detailed excitation spectra are presented in [12]. The spectra measured in the STW under the excitation in Pr^{3+} absorption bands were similar to the STW spectra measured under X-ray excitation. On the contrary, the signal was very low in the LTW in SrF_2-Pr^{3+} and BaF_2-Pr^{3+}, and only a faint hint on the *5d-4f* emission could be observed in the LTW for CaF_2-Pr^{3+} (curve 2 in Figure 3).

The spectra measured in the LTW were essentially different under the excitation in the STE emission band of a crystal at 9.93 eV for the BaF_2-Pr^{3+} and at 10.33 eV for the SrF_2-Pr^{3+} and CaF_2-Pr^{3+} (Figure 4). The broad non-structured STE emission bands appeared in the spectra of SrF_2-Pr^{3+} and BaF_2-Pr^{3+}. Their positions were close to those of the STE emission bands under X-ray excitation. Unexpectedly, an explicit structure connected with the *5d-4f* emission
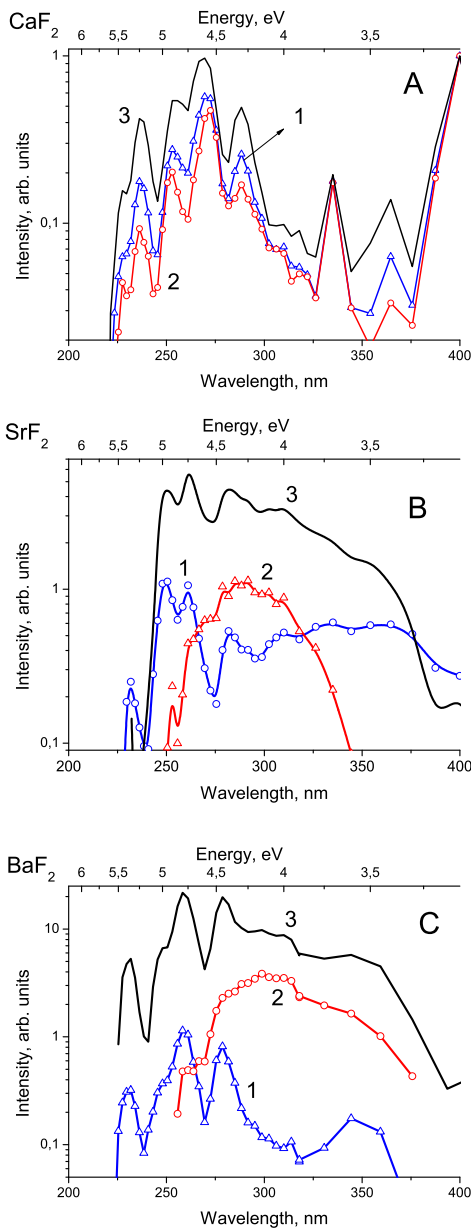
Figure 1. Time-resolved spectra under pulsed X-ray excitation at 80 K of CaF_2–0.1 mol.% PrF_3 , SrF_2–0.1 mol.% PrF_3 and BaF_2–0.1 mol.% PrF_3 (1 - short time window (0-12 ns); 2 - long time window (100-200 ns); 3 - time-integrated)
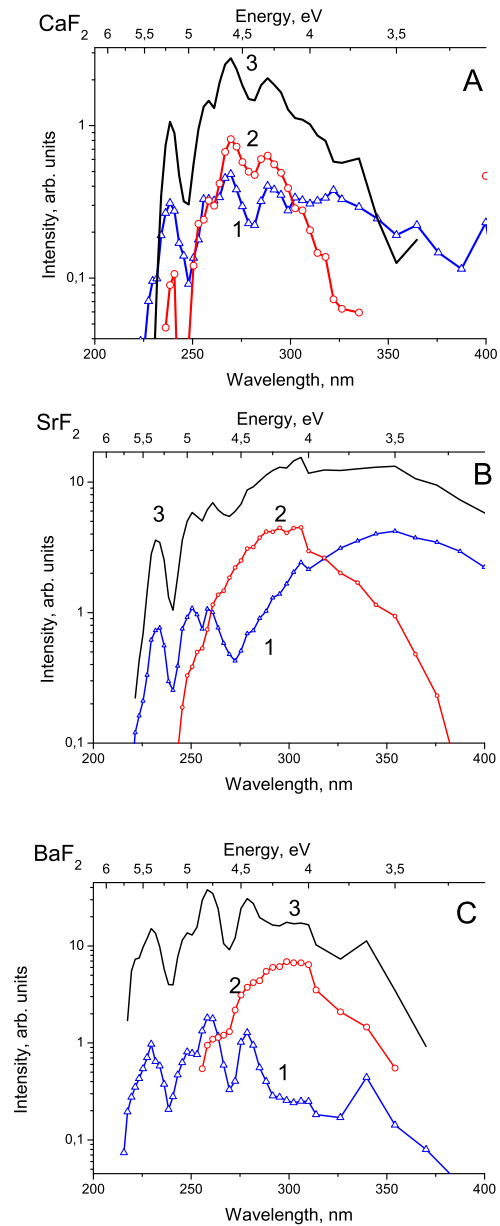
Figure 2. Time-resolved spectra under pulsed X-ray excitation at 80 K of CaF_2–1 mol.% PrF_3 , SrF_2–1 mol.% PrF_3 and BaF_2–1 mol.% PrF_3 (1 - short time window (0-12 ns); 2 - long time window (100-200 ns); 3 - time-integrated)
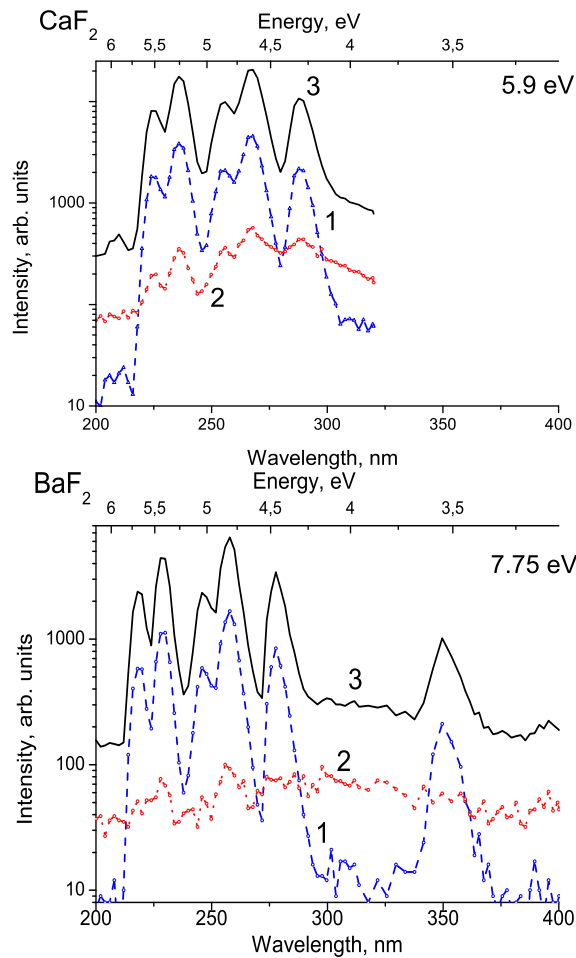
was observed in the LTW for SrF_2-Pr^{3+} and CaF_2-Pr^{3+} (curves 2, 3 in Figure 4).

3.2. Decay times

The decay times of Pr^{3+} emission measured for CaF_2-Pr^{3+}, SrF_2-Pr^{3+}, and BaF_2-Pr^{3+} crystals at room temperature and 80 K under pulsed X-ray excitation and at 11 K under excitation by

Figure 3. Time-resolved spectra under synchrotron excitation of CaF_2–0.1 mol.% PrF_3 and BaF_2–0.1 mol.% PrF_3 (1 - short time window (1.5-10.5 ns); 2 - long time window (114-162 ns); 3 - time-integrated) at 11 K
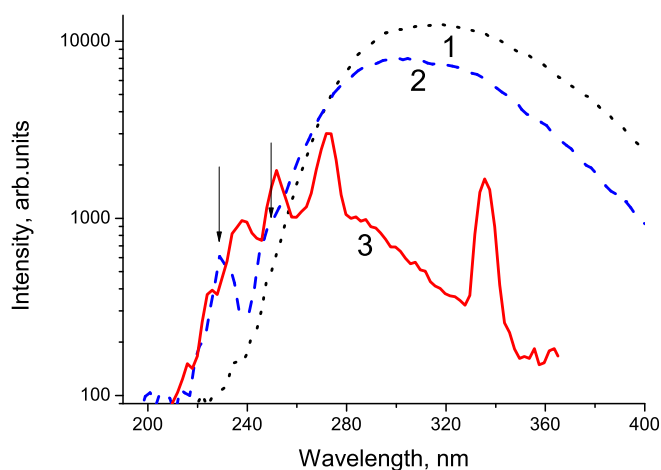
Figure 4. Long time window emission of BaF_2 (curve 1), SrF_2 (curve 2) and CaF_2 (curve 3) doped with 0.1% Pr^{3+} excited in STE excitation bands (9.93 eV for BaF_2 and 10.33 eV for SrF_2 and CaF_2.

synchrotron radiation are compared in Table 1.

Under the excitation by synchrotron radiation, one dominant fast component with the decay time 25, 24 and 21 ns was detected in the *5d-4f* emission of CaF_2-Pr^{3+}, SrF_2-Pr^{3+} and BaF_2-

Table 1. Decay times of the *5d-4f* emission of Pr^{3+}-doped alkali-earth fluorides.

	X-ray excitation (80 K)	X-ray excitation (RT)	Synchrotron excitation (11 K)[0]
BaF_2	4-5 ns (>0.3 mol.% Pr^{3+}) 21-22 ns	7-8 ns (>0.1 mol.% Pr^{3+}) 28 ns	– 21 ns
SrF_2	8 ns (>0.3 mol.% Pr^{3+}) 24 ns $\approx$300 ns	10 ns (>0.1 mol.% Pr^{3+}) 32 ns	8 24 ns
CaF_2	32 ns $\approx$250 ns	40 ns	25 ns

[0] Measurement of decay time under synchrotron excitation was performed at 5.9 eV in $CaF_2 – Pr^{3+}$, 6.53 eV in $SrF_2 – Pr^{3+}$, and 5.77 eV in $BaF_2 – Pr^{3+}$
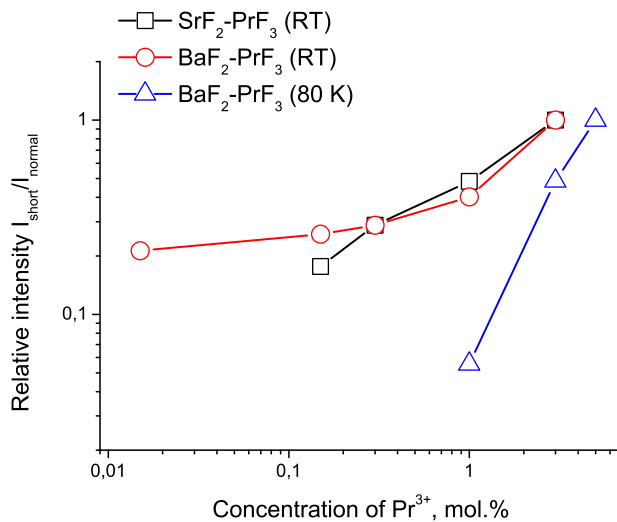
Figure 5. Concentration dependence of the intensity ratio of the faster component to the normal one of the *5d-4f* Pr^{3+} emission in SrF_2 and BaF_2

Pr^{3+}, respectively (Table 1). Two fast components were detected in the *5d-4f* emission of Pr^{3+}-doped BaF_2 and SrF_2 under X-ray excitation. The decay time of the faster one was 4-5 ns in $BaF_2 – Pr^{3+}$ and 8 ns in $SrF_2–Pr^{3+}$ at 80 K. The second somewhat slower component (21 ns in BaF_2-Pr^{3+} and 24 ns in SrF_2-Pr^{3+}) possess the decay time typical of Pr^{3+} in other fluorides [4], [16] and can be regarded as a normal emission decay component of a single Pr^{3+} ion.

The faster component had higher intensity in the crystals doped with larger concentrations of Pr^{3+} (>0.3 mol%) and in higher-energy emission bands. It becomes more intensive at higher temperatures, and, therefore, at room temperature can be detected in the crystals with Pr^{3+} concentrations lower than 0.3%. The concentration dependence of the relative intensity of the faster decay component is given in Figure 5. The relative intensity was taken as the ratio of the intensity of the faster component to that of the normal component in the *5d-4f* emission of Pr^{3+}. The curves in Figure 5 are normalized to the maximum. We did not find a spectral shift of the faster component with respect to the position of a normal component in SrF_2-Pr^{3+} and BaF_2-Pr^{3+}. Under the excitation by synchrotron radiation, the faster component was found only in SrF_2-Pr^{3+}. Only one fast component with the decay time 32 ns was detected under X-ray excitation in CaF_2-Pr^{3+}. However, a second remarkably longer component of about 250 ns was found in it. A weak long component of about 300 ns was found also in SrF_2-Pr^{3+}.

4. Discussion

The presence of the *5d-4f* Pr^{3+} emission in the LTW in the conditions of a direct excitonic excitation indicates that the 5d states of Pr^{3+} are populated due to the excitonic energy transfer mechanism at low temperatures in SrF_2 and CaF_2 doped with Pr^{3+}. Self-trapped excitons (STE) emitting at 300 nm [15] could be regarded as possible candidates for the energy transfer. Indeed, energy transfer by STEs has been proven to be a predominant mechanism in fluorides doped with Ce^{3+} [17], [19]. Participation of STEs in energy transfer to the impurity ion has been suggested in lutetium orthoaluminate doped with Pr^{3+} [18]. However, no dependence of the transfer efficiency on cation has been found in the fluorides doped with Ce^{3+} [17], [9]. At the same time, it depends considerably on cation in Pr doped fluorides, whereas the transfer is the most efficient in CaF_2-Pr^{3+} and almost negligible in BaF_2-Pr^{3+} (Figure 4). Finally, the *d-f* emission energies are higher than the STE band in the fluorides doped with Pr. Thus, the possibility of energy transfer from the host to Pr^{3+} center by self-trapped excitons can be set aside for Pr doped fluorides.

Another excitonic emission band situated approximately 1 eV higher than the well-known STE emission in calcium and strontium fluorides has been reported in [20]. It is almost indistinguishable in pure crystals, but becomes more prominent in doped crystals, where the STE emission is partly suppressed. It has been shown that this emission belongs to the off-centre excitons [20]. The emission band of the off-center exciton overlaps with the *5d-4f* emission of Pr^{3+}, that might facilitate the energy transfer to a Pr-center by the off-centre exciton. These excitons are quenched at about 150 K, therefore, such a transfer mechanism does not work at room temperature. Finally, the excitation energy transfer by off-centre excitons takes obviously place in Pr^{3+} doped SrF_2 and CaF_2. In CaF_2-Pr^{3+}, this mechanism becomes the dominant one at low temperatures.

The absence of a slow component in the *5d-4f* emission of BaF_2-Pr^{3+} under the conditions of a direct creation of excitons by synchrotron radiation indicates that no energy transfer from excitons to Pr^{3+} ions occurs. Under X-ray excitation, the emission is efficient, but only the fast component of the *5d-4f* luminescence is observed. It allows us to conclude that the energy transfer mechanism is fast. In the previous studies of barium fluorides [7] and LuAG [21] doped with Pr^{3+} such mechanism has been called as "consecutive capture and recombination of charge carriers". The process is based on the energy transfer from an e-h pair to a Pr^{3+} ion. The capture of a hole seems more favorable, since Pr is stable in a tetravalent state. Other fast mechanisms can also play a role. It has been shown, for instance, that the excitation of the *5d-4f* emission can be stimulated by the core-valence luminescence in barium fluoride crystals doped with Pr^{3+} [12].

We also found a non-linear concentration dependence of the faster component of Pr luminescence in BaF_2-Pr^{3+} and SrF_2-Pr^{3+} (Figure 5). The ability of Pr^{3+} to form easily aggregates in strontium fluoride has been shown in [22]. Consequently, aggregates of Pr^{3+} ions might be the cause of these faster components in such crystals. However, it remains uncertain, why a faster component is not found in CaF_2-Pr^{3+}.

5. Conclusions

The emission of Pr^{3+} doped CaF_2, SrF_2, and BaF_2 crystals was studied under synchrotron and X-ray excitation. Aggregates of Pr^{3+} ions, which cause additional fast components in the emission decay kinetics, were found in SrF_2 and BaF_2 crystals doped with Pr^{3+} in concentration higher than 0.1 mol.%. Based on the observation of slow components in Pr^{3+} luminescence energy transfer from excitons to Pr^{3+} ions was shown in Pr^{3+} doped CaF_2 and SrF_2.

Acknowledgments

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